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16. ABSTRACT

Recent 1982 measurements of the nonmethane organic compound (NMOC) are reported for the Lincoln Tunnel. The NMOC levels in the tunnel were a factor of approximately 4 lower than 1970 levels. This decrease probably reflects reduced vehicular tailpipe emissions due to EPA hydrocarbon control strategy for photochemical ozone. Acetylene contribution to the total NMOC composition decreased almost by a factor of 2 from 1970 to 1982. This decrease was attributed to the preferential oxidation of acetylene by the vehicular catalytic device. New hydrocarbon component and sum of NMOC component ratios to acetylene are presented. These ratios are useful in the determination of hydrocarbon source emission contribution in urban and industrial areas.

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Non-Methane Organic Composition in the Lincoln Tunnel

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■ Measurements of the non-methane organic carbon (NMOC) are reported for the Lincoln Tunnel from a 1982 study. The NMOC levels in the tunnel were a factor of approximately 4 lower than those found in a similar study performed in 1970. This decrease probably reflects reduced vehicular tailpipe emissions due to the utilization of catalyst-equipped vehicles. Acetylene concentrations in the tunnel decreased to a greater extent than many of the other major individual hydrocarbon compounds during the 1970–1982 period. This decrease was attributed to the preferential oxidation of acetylene by the catalytic converter installed on vehicles beginning with the 1975 model year. New NMOC compounds and sum of NMOC compounds to acetylene ratios are reported. These ratios are useful in the estimation of the vehicular tailpipe emission contribution to NMOC levels observed in urban and industrial areas.

Introduction

In 1974 ratios of individual non-methane organic carbon (NMOC) compounds and sum of individual NMOC compounds to acetylene ratios were reported for a Lincoln Tunnel study performed in 1970 (*1*). It was pointed out at that time that these ratios were useful for estimating vehicular tailpipe contribution to the NMOC air quality of urban, suburban, and industrial areas. Acetylene was used for these ratios since it is nearly unique to the vehicular combustion process. Also acetylene possesses a long atmospheric lifetime of approximately 150 days which is important for its use as a vehicular tracer. A tunnel was selected as the sampling location to determine these ratios since it is dominated by vehicular tailpipe emissions. It is also thought that the tunnel atmosphere is representative of a large number of vehicles and fuel types used in typical urban areas. Since that time others have used tunnel sampling for much the same reasons. Hampton et al. (*2*) used gas chromatography/mass spectrometry (GC/MS) to identify the presence of more than 300 organic compounds emitted by gasoline- and diesel-powered engines in the Allegheny Mountain Tunnel along the Pennsylvania Turnpike. In the same study Pierson et al. (*3*) used the tunnel atmosphere to collect filter samples to evaluate bacterial mutagenicities of particulate emissions from heavy-duty diesel and gasoline-powered vehicles. Hampton et al. (*4*) calculated emission rates of 22 gas-phase hydrocarbon (HC) compounds in the tunnel atmosphere and compared these results to those made from dynamometer studies. Others have used tunnels to look at the optical properties of aerosol-phase material emitted by vehicles (*5*, *6*).

Starting with the 1975 model year, catalytic converters have been installed on automobiles to reduce NMOC exhaust emissions. However, catalyst-equipped vehicles require unleaded fuels for proper operation. These unleaded fuels are prepared by adjusting NMOC compositions to obtain a suitable octane rating instead of using the tetraethyl lead additive. It was projected that for 1982 the mean age of the U.S. passenger car fleet was 7.4 years and that nearly 55% of the in-use passenger car fleet consisted of 1975 and later-model-year vehicles (*7*). Likewise in 1982, the national sales of unleaded fuel, required for catalyst-equipped vehicles, contributed almost 60% of total gasoline sold (*8*). Such drastic changes in vehicles and gasoline types are expected to have had a significant impact on vehicular tailpipe NMOC composition, likewise, on the NMOC compounds and sum of NMOC compounds to acetylene ratios. Indeed Black and High (*9*) and Jackson (*10*) have reported significant differences in HC composition between catalytic-converter-equipped and -nonequipped automobiles from dynamometer simulations of roadway driving conditions. Jackson (*10*) reported an average HC for nonconverter-equipped cars of 33.4% paraffin, 26.6% olefin, and 32.1% aromatic. The HC composition for catalytic-converter-equipped cars averaged 56.5% paraffin, 15.5% olefins, and 26.2% aromatic (*10*). Black and High's (*9*) results indicated large variation in percent paraffin, olefin, and aromatic composition for various types of control system devices, e.g., lean combustion and oxidation catalysts. Their data also show low olefin content in the exhaust of catalytic-converter-equipped vehicles. Both Black and High (*9*) and Jackson (*10*) reported significant decreases in percent acetylene contribution to HC totals for catalytic-converter-equipped cars. Acetylene percentages decreased from 7.9% to 2.2% (*10*).

The existing literature supports the contention of suspected changes in vehicular tailpipe NMOC composition with the introduction of catalyst-equipped vehicles. Most particularly the acetylene levels released by vehicular tailpipe emissions have significantly decreased. Consequently, published NMOC compound and sum of NMOC compounds to acetylene ratios are not appropriate for current urban and industrial ambient air applications. The purpose of this paper is to present more recent tunnel NMOC compositional analyses and more current NMOC compounds and sum of NMOC compounds to acetylene ratios. The relationship between the tunnel NMOC composition and an averaged NMOC composition determined from the analyses of selected local gasolines is also presented. It is thought that the presented tunnel NMOC composition and ratios to acetylene are more representative of the existing vehicular fleet composition. It is also anticipated that these NMOC compounds and sum of NMOC compounds to acetylene ratios are useful for source reconciliation and photochemical ozone control applications.

Experimental Section

The Lincoln Tunnel is situated under the Hudson River and connects Weehawhen, NJ, with Manhattan Island. The Tunnel complex consists of three tubes referred to as north, south, and center. Traffic flow from Manhattan Island to New Jersey and vis-à-vis is routed differently through these tubes depending upon the time of day. An automated sample collection device was located along the tunnel catwalk of the center tube near the tunnel ventilation tower. This location is approximately 200 ft from the New Jersey side tunnel entrance. Thirty-minute integrated samples were collected in 2-mil Tedlar bags (E.

I. du Pont Corp., Wilmington, DE) for the 7:30–8:00 a.m., 8:00–8:30 a.m., 8:30–9:00 a.m., and 9:00–9:30 a.m. time periods from September 3 to September 9, 1982. These time periods corresponded to the busiest morning traffic density. Actual traffic densities through the center tube for the 7:00–9:00 a.m. period during September 3–9, 1982, ranged from 1300 to 2700 vehicles/h with an average density of about 2000 vehicles/h (*11*). Vehicular composition passing through the tunnel is not determined (*11*). However, visual inspection of the traffic moving through the tunnel during the sample collection period suggested a vehicular mixture dominated by light-duty passenger automobiles. Collected samples were transferred to 6-L surface passivated stainless steel canisters (Demaray Scientific Instruments, Ltd., Pullman, WA) for storage and transported back to the laboratory for detailed gas chromatographic (GC) analyses.

Duplicate 120-min integrated samples of the outside air used by The Port Authority of New York and New Jersey Tunnel to ventilate the tunnel chambers were also collected during the 7:30–9:30 a.m. period. These samples were also transferred to 6-L stainless steel canisters and transported back to the laboratory for detailed analyses.

Detailed hydrocarbon analyses of five local area leaded and unleaded gasolines were performed. Vapor-phase samples of the gasolines were prepared by the injection of 1 μL of the liquid into 2-mil Tedlar bags containing 50-L of zero hydrocarbon air. The gasolines analyzed included the regular and unleaded brands of Exxon, Sunoco, Amoco, Mobil, and Getty. The extra unleaded brand of Exxon and the super unleaded brand of Sunoco were also analyzed.

The GC procedures used for the C_2–C_{10} hydrocarbon analysis are quite similar to those used for the 1970 Lincoln Tunnel Study (*1*). A three GC column system was used to analyze the C_2–C_5 aliphatic, the C_4–C_8 aliphatic, and the C_6–C_{11} aromatic and aliphatic compounds. The columns that wore out from usage over the 12-year period were replaced with nearly identical substitutions. The original 0.15 cm i.d. open tubular columns used for the C_4–C_8 aliphatic and C_6–C_{10} aromatic analysis were replaced with similar theoretical plate 0.05 cm i.d. SCOT columns. The same packed silica gel column, used for the C_2–C_5 aliphatic analysis, was used for both studies. Detailed description of the GC columns used for the 1982 study is published elsewhere (*12*). The sample preconcentration technique used for this study was improved from the 1970 study to accommodate larger and variable size samples (*13*).

All three GC columns were calibrated with a National Bureau of Standards (NBS) 2.84 ppm of propane in air–Standard Reference Material (SRM) No. 1665b cylinder. Diluted calibration samples of the NBS–SRM mixture were prepared with a TECO Model 101 dilution system (TECO Corp., Whatham, MA). A single response factor was determined for each GC–FID column system and was used to calculate individual NMOC component concentrations as parts per billion of carbon (ppb of C). This approach has been demonstrated to be valid for NMOC compounds (*14*).

Precision of the GC procedure was determined by the duplicate analyses of collected samples. An example of the precision obtained can be demonstrated for the outside tunnel ventilation air samples where 40% of the average 110 GC peaks measured duplicated to within ±2% of the respective mean concentration. More than 65% of the GC peaks duplicated to within ±10% of the respective mean concentrations. Approximately 95% of the 110 GC peaks measured above 2.0 ppb of C duplicated to within ±10% of the respective mean concentration. The concentration of the individual GC peaks measured in these samples ranged from 0.1 to 71.3 ppb of C. Similar statistics were observed for duplicate analyses of the tunnel air samples. The concentration of the 140 individual GC peaks in the tunnel samples ranged from 0.1 to 518.0 ppb of C.

Formaldehyde and acetaldehyde analyses were also performed on the collected tunnel and outside air bag samples. The Tedlar bag was considered to be an adequate container for formaldehyde and acetaldehyde for the short 4–5-h storage period required in this study (*15*). The aldehydes were analyzed as their 2,4-dinitrophenylhydrazone (DNPH) derivatives by high-performance liquid chromatography (HPLC). Specific details of the HPLC system concerning column type, mobile phase, and other information are published elsewhere (*16*). A 10-L volume of the air sample bag was pulled through a solution containing DNPH in acetonitrile. An aliquot of the collected solution was placed in a 2-cm^3 sample vial, sealed, and returned to the Research Triangle Park, NC, laboratory for HPLC analysis. Calibration standards for formaldehyde and acetaldehyde were prepared by dissolving weighed amounts of the purified formaldehyde–DNPH and the acetaldehyde–DNPH derivatives in a known volume of acetonitrile reagent. Aliquots of these calibration standards were periodically injected onto the HPLC during the analyses of the tunnel samples.

Analyses for NO and NO_x were performed with a Monitor Labs Model 8440 NO chemiluminescent analyzer (Monitor Labs, Inc., San Diego, CA). These analyses were made from the tunnel and outside air Tedlar bag samples. The NO chemiluminescent instrument was calibrated with a NBS traceable 98.7 ppm of NO in nitrogen standard gas mixture (AIRCO Co., Murray Hill, NJ). Diluted calibration samples of the NO in nitrogen standard were prepared with the TECO Model 101 dilution system.

CO analyses were also made of the tunnel and outside air bag sample with a TECO Model 48 CO infrared analyzer (TECO Corp., Watham, MA). The CO analyzer was calibrated with an NBS-traceable 102 ppm of CO in nitrogen standard gas mixture (Scott Specialty Gases, Plumbsteadville, PA).

Results and Discussion

Comparison of NMOC Compositions from 1970 and 1982 Tunnel Studies. Average concentrations and standard deviations are given in Table I for selected NMOC compound and sums of NMOC compounds measured in the 1982 and 1970 Lincoln Tunnel studies. The 25 HC compounds listed in Table I were selected on the basis of abundance and representation of the range of C_2–C_{10} NMOC compounds found in the tunnel samples. In the 1982 study, 60 identified and 80 unidentified compound peaks were observed on the GC systems. The 60 identified peaks represented approximately 84% of the total NMOC mass measured in the tunnel samples. All 140 GC peaks measured are represented in the sum of paraffins, olefins, and aromatics. Assignment of the 80 unidentified peaks as paraffins, olefins, and aromatics was made by retention times and the use of chemical stripper columns (*17*, *18*) with selected tunnel samples. The stripper columns selectively remove olefins and aromatic compounds from complex hydrocarbon mixtures. The Ag_2SO_4–H_2SO_4 stripper column removed all aromatics (except benzene which is approximately 60% removed). The $HgSO_4$–H_2SO_4 stripper column removed all olefinic compounds. Compounds not removed by either stripper column were assumed to be paraffins.

To compare the average concentrations obtained from the two studies, ratios of the 1970–1982 results are also

Table I. Averaged Concentration for Selected NMOC Compounds and Sum of NMOC Compounds in Parts per Billion of Carbon (ppb of C) for 1982 and 1970 Lincoln Tunnel Studies

compound	1982 concn ± SD	1970 concn ± SD	ratio 1970/1982
ethylene	408.7 ± 72.4	1374.9 ± 307.2	3.4
acetylene	160.7 ± 46.0	1033.0 ± 197.2	6.2
propylene	122.4 ± 18.8	630.1 ± 144.9	5.1
isobutane	76.4 ± 12.9	413.7 ± 99.4	5.4
n-butane	198.1 ± 37.0	998.8 ± 229.7	5.0
isobutylene + *n*-but-1-ene	89.1 ± 15.9	344.9 ± 64.3	3.9
sum of C_4 olefins	133.8 ± 26.0	614.1 ± 117.8	
isopentane	305.3 ± 60.6	1296.7 ± 298	4.2
n-pentane	145.9 ± 30.7	639.9 ± 135.0	4.4
n-pent-1-ene	15.8 ± 3.2	69.2 ± 12.9	4.4
sum of C_5 olefins	131.7 ± 27.3	582.9 ± 136.0	4.4
3-methylpentane	73.8 ± 12.6	350.2 ± 84.6	4.7
n-hexane	74.8 ± 14.2	373.4 ± 86.0	5.0
n-hex-1-ene	14.6 ± 2.9	30.8 ± 6.9	2.1
2,4-dimethylpentane	68.9 ± 12.0	355.0 ± 83.6	5.1
cyclohexane	45.6 ± 13.9	57.3 ± 13.0	1.3
3-methylhexane	49.7 ± 9.8	249.1 ± 54.2	5.0
2,2,4-trimethylpentane	56.6 ± 10.9	275.3 ± 59.4	4.9
benzene	202.2 ± 33.7	1182.5 ± 470.0	5.8
toluene	303.4 ± 55.5	1286.4 ± 200.2	4.2
p-xylene	48.6 ± 9.0	251.5 ± 36.1	5.2
m-xylene	114.1 ± 20.8	709.3 ± 171.0	6.2
o-xylene	74.3 ± 15.2	290.6 ± 57.3	3.9
p- + *m*-ethyltoluene	92.4 ± 16.1	381.1 ± 41.2	4.1
1,3,5-trimethylbenzene	26.7 ± 4.9	131.5 ± 26.4	4.9
formaldehyde	57.4 ± 13.1		
acetaldehyde	11.0 ± 6.0		
sum of paraffins	1678.1 ± 303.5	7052.8 ± 1678.0	4.2
sum of olefins	940.3 ± 158.3	3399.7 ± 705.0	3.6
sum of aromatics	1516.4 ± 319.4	5061.3 ± 1060.1	3.3
sum of NMOC	4295.8 ± 695.9	16547.2 ± 3640.9	3.9
NO_x	2416 ± 627	6290 ± 2280	2.6
carbon monoxide	15600 ± 3800	65800 ± 14900	4.2
NMOC/NO_x	1.77	2.63	

presented in Table I. Significantly lower average concentrations were observed in the 1982 study than during the 1970 investigation. The factor of approximately 4 difference for most NMOC compounds and sum of NMOC compounds probably reflects the impact of automobile HC control strategy over the 12-year period. Tunnel air ventilation rates and vehicular traffic densities are not expected to have changed significantly over this time period. Tunnel air ventilation rates have not been permanently altered during the 12-year period (*19*). Ventilation rates are, however, adjusted at high traffic densities in order to maintain acceptable levels of visibility and carbon monoxide for health-related reasons (*19*). The factor of approximately 4 is consistent with the change in vehicular composition between 1970 and the 1982 fleet of catalyst-controlled and -uncontrolled automobiles and the resulting averaged NMOC emission rates expected (*20*).

Changes in the NMOC composition over the 12-year period are not particularly different. The most abundant compounds observed in the 1982 study were nearly similar to those found in the 1970 study. Ethylene is the most abundant NMOC compound found in both tunnel studies. Isopentane and toluene have similar concentrations and are the next most abundant NMOC compounds found in tunnel air for both the 1970 and 1982 studies. Some NMOC compounds changed less significantly than others. For example, cyclohexane concentration was approximately the same in both tunnel studies. Acetylene and *m*-xylene concentrations changed most significantly over the 12-year period. Very likely the significant change in acetylene concentration from 1970 to 1982 is due to the presence of catalyst-equipped automobiles and the reported preferential oxidation of the acetylene compound by the catalytic surface (*9*, *21*). However, the similar significant drop of *m*-xylene concentration over the 12-year period may have resulted from changes in gasoline compositions instead of selective catalytic oxidation.

In the 1982 study, the GC separation of benzene was improved over that made in 1970. In the 1970 study, accurate benzene determination could not be made due to the presence of interfering paraffinic compounds. Consequently the 1970 average benzene concentration in Table I is not accurate and was included only for comparison to the 1982 value.

Composition of total paraffins, olefins, aromatics, and acetylene did change somewhat over the 12-year period. In 1970 the percent paraffin, olefin, aromatic, and acetylene composition was 42.6, 20.5, 30.6, and 6.3, respectively. The 1982 percent paraffin, olefin, aromatic, and acetylene composition was 39.1, 21.8, 35.3, and 3.7, respectively. The most significant changes in NMOC composition occurred in the aromatic and acetylene fractions. Surprisingly the olefins fraction showed the least change over the 12-year period. A decreased olefinic fraction was expected since dynamometer studies of Black and High (*9*) and Jackson (*10*) reported low olefin levels from tailpipe emissions of catalyst-equipped vehicles. These researchers (*9*, *10*) concluded preferential oxidation of the olefinic compounds by the catalytic surfaces. The tunnel olefin fraction slightly increased in 1982 even though a significant percentage of the in-use automobile fleet was comprised of catalyst-equipped vehicles (*7*). The 1982 results suggest that the catalysts are not effective for the selective removal of the olefinic compounds. Indeed, Jackson (*10*) reported a deteriorated performance of the catalyst for the removal of olefinic HCs as mileage accumulated on the test vehicles used for the dynamometer studies. It is likely that the majority of catalyst-equipped vehicles traveling through the tunnel have accumulated significant mileage and have lost their effectiveness for the selective removal of the olefinic HC's. Catalyst-equipped vehicles operating under a fuel-rich condition can also alter exhaust emission composition (*21*) and may explain at least part of the high olefin content observed in the 1982 tunnel results. Carburetion changes of in-use vehicles can occur without a proper vehicular maintenance program.

Formaldehyde and acetaldehyde were analyzed for in the 1982 study but not in the 1970 investigation. A comparison of concentration variation over the 12-year period cannot be determined. The average formaldehyde to acetaldehyde concentration ratio of 5.2 observed in the tunnel is more than double the 2.3 value recently reported for dynamometer-tested 1975–1982 vehicles (*22*). However, the 1.6% contribution that the combined aldehydes make to the tunnel NMOC burden is well within the 0.8–6.6% range reported for the 46 in-use passenger cars using three different dynamometer test cycles.

Comparison of NMOC Composition for the Tunnel with Local Gasolines. Most of the NMOC compounds found in vehicular tailpipe exhaust are also present in gasolines. Acetylene, ethylene, and propylene are not found in gasolines and are produced in the oxygen-deficient combustion process of the automobile internal combustion engine (*23*). To compare tunnel and fuel NMOC compositions, commerical brands of locally sold leaded and unleaded gasolines were analyzed. Five major commercial

Table II. Average Percentage Composition of Selected NMOC and Sum of NMOC to Total NMOC for Three Blends of Gasoline Sold in the New York–New Jersey Area along with the NMOC Composition Observed in the 1982 Lincoln Tunnel

component	leaded	unleaded	super unleaded	tunnel
sum of paraffins	72.1 ± 10.9	61.6 ± 9.4	56.7 ± 3.4	40.9
sum of olefins	9.2 ± 0.49	11.5 ± 2.7	7.5 ± 0.4	23.0
sum of aromatics	18.8 ± 11.5	26.9 ± 10.9	35.8 ± 3.1	36.1
benzene	1.4 ± 0.83	1.7 ± .6	4.6 ± 3.2	4.7
toluene	2.8 ± 2.3	5.1 ± 1.0	9.6 ± 1.1	7.1
m-xylene	1.9 ± 1.3	2.9 ± 1.2	3.6 ± 0.2	2.7
o-xylene	1.1 ± 0.69	1.6 ± 0.6	2.2 ± 0.1	1.7
1,3,5-trimethylbenzene	0.5 ± 0.3	0.7 ± 0.3	2.1 ± 2.1	0.66
1,2,4-trimethylbenzene	1.6 ± 1.0	2.3 ± 1.0	1.6 ± 1.1	2.2
isopentane	12.7 ± 1.6	12.0 ± 1.2	10.0 ± 0.3	7.1
n-butane	4.2 ± 1.3	5.8 ± 2.2	5.7 ± 1.7	4.6
3-methylpentane	4.5 ± 0.8	3.4 ± 0.5	2.4 ± 0.64	1.7
2,2,4-trimethylpentane	1.7 ± 1.0	3.3 ± 1.1	6.5 ± 2.5	1.3
isobutylene + *n*-but-1-ene	0.41 ± 0.08	0.50 ± 0.12	0.38 ± 0.9	2.1
trans-but-2-ene	0.45 ± 0.15	0.66 ± 0.22	0.46 ± 0.13	0.57
cis-pent-2-ene	1.58 ± 0.33	1.97 ± 0.44	1.14 ± 0.21	1.27
n-hex-1-ene	0.39 ± 0.10	0.73 ± 0.43	0.26 ± 0.05	0.34

brands were selected on the basis of the observed abundance of these service station facilities. The gasoline brands included Exxon, Mobil, Amoco, Getty, and Sunoco. It was later determined that this was a prudent selection of gasolines since these brands commanded a large share of market sales for the New York–New Jersey area in 1982 (*24*). Average compositional results for the five brands of gasoline are given in Table II. Significant differences are observed in the average compositions of the three grades of gasoline, most noticeably between the percent paraffinic and aromatic fractions. The average composition of the leaded blend is most abundant in paraffins, while the average composition of the super unleaded blend is most abundant in percent aromatics. The average percent paraffins and aromatics composition of the unleaded blend falls in between those of the leaded and the super unleaded blends. These observations are consistent with the blending procedures used by gasoline manufacturers for the preparation of unleaded fuels. The higher octane aromatic fraction is increasd to compensate for the elimination of the tetraethyllead additive. The average composition representative of gasoline usage during 1982 is expected to fall somewhere between the leaded and unleaded blends (*8*).

The individual NMOC compounds listed in Table II were selected from the 60 identified compounds observed in the gasoline analyses. These compounds were selected from relative abundance and are intended to be representative of the C_4–C_{10} mixture of the NMOC compounds found in these gasolines. The actual NMOC composition in the tunnel is significantly different from any of the gasoline blends. Large differences occur in the sum of paraffins and the sum of olefin percentages. The sum of olefin percentage in the tunnel more than doubles that of the gasolines, mostly at the expense of the paraffins. Ethylene and propylene, neither of which is found in gasoline, account for the majority of this increase. Toluene is the most abundant aromatic compound in each of the analyzed gasoline blends. However, with the exception of the super unleaded blend, the percent toluene of total NMOC in tunnel air is higher than in the uncombusted fuels. On the other hand, isopentane, the most abundant paraffin NMOC compound, decreases in relative abundance from the gasoline fuels to the tunnel air. These observations suggest that isopentane combusts more efficiently in both the engine and the vehicular catalytic system than does toluene. To investigate this aspect more thoroughly, ratios of the NMOC compounds and sum of NMOC compounds to toluene and isopentane were determined. These ratios are given in Tables III and IV.

Table III. Selected NMOC and Sum of NMOC Ratios to Toluene for Three Blends of Gasoline Sold in the New York–New Jersey Area along with Similar Ratios for the 1982 Lincoln Tunnel Results

component	leaded	unleaded	super unleaded	tunnel
sum of paraffins	25.5	12.1	5.9	5.8
sum of olefins	3.3	2.3	0.78	3.2
sum of aromatics	6.7	5.3	3.7	5.1
benzene	0.50	0.33	0.48	0.66
toluene	1.0	1.0	1.0	1.0
m-xylene	0.68	0.57	0.38	0.38
o-xylene	0.39	0.31	0.23	0.24
1,3,5-trimethylbenzene	0.18	0.14	0.22	0.08
1,2,4-trimethylbenzene	0.57	0.45	0.17	0.31
isopentane	4.5	2.4	1.0	1.0
n-butane	1.5	1.1	0.59	0.65
3-methylpentane	1.6	0.67	0.21	0.24
2,2,4-trimethylpentane	0.61	0.65	0.68	0.18
isobutylene + *n*-but-1-ene	0.15	0.10	0.04	0.29
trans-but-2-ene	0.16	0.13	0.05	0.08
cis-pent-2-ene	0.56	0.37	0.12	0.18
n-hex-1-ene	0.14	0.14	0.03	0.05

The NMOC compounds and sum of NMOC compounds to toluene ratios given in Table III reemphasize the significant changes in the NMOC composition from the fuel to the combustion products of the tailpipe emissions. Ratios to toluene for both individual paraffinic compounds and sum of paraffinic compounds are particularly lower in tunnel air than in either the leaded or unleaded blends of gasolines. The results suggest that in reference to toluene the paraffinic compounds are most significantly affected by the combustion processes. The sum of olefin to toluene ratios are similar in both fuel and tunnel compositions. Since the results listed in Table II indicate a significant increase of olefin fraction in the combusted NMOC composition, it appears either that toluene is more resilient than other NMOC compounds in the combustion processes or that it is produced by the alkylation–dealkylation processes of the aromatic compounds that occur in the internal combustion engine. The increased benzene to toluene ratio in tunnel air over that of the fuels suggests that benzene is also resilient to the combustion process and is also produced in the dealkylation process of the substituted aromatics. The combined isobutylene and but-1-ene component is the only olefinic NMOC listed in Table III that showed an increased abundance relative to toluene in the tunnel air compared to the fuels. The other olefinic NMOC compounds listed in Table III demonstrate a decreased abundance relative to toluene. This suggests that these two C_4 olefins are produced in the combustion process along with ethylene and propylene.

The ratios to isopentane for the NMOC compounds and sum of NMOC compounds in Table IV reinforce the observations previously made for Table III results. It appears that all the paraffinic NMOC compounds listed in Table IV decrease similarly to isopentane in the tunnel air compared to the fuels. The sum of olefinic NMOC compound

Table IV. Selected NMOC and Sum of NMOC Ratios to Isopentane for Three Blends of Gasoline Sold in the New York–New Jersey Area along with Similar Ratios for the 1982 Lincoln Tunnel Results

component	leaded	unleaded	super unleaded	tunnel
sum of paraffins	5.7	5.1	5.7	5.8
sum of olefins	0.72	0.96	0.75	3.2
sum of aromatics	1.5	2.2	3.6	5.1
benzene	0.11	0.14	0.46	0.66
toluene	0.22	0.43	0.96	1.0
m-xylene	0.5	0.24	0.36	0.38
o-xylene	0.09	0.13	0.22	0.24
1,3,5-trimethylbenzene	0.04	0.06	0.21	0.08
1,2,4-trimethylbenzene	0.13	0.19	0.16	0.31
isopentane	1.0	1.0	1.0	1.0
n-butane	0.33	0.48	0.57	0.65
3-methylpentane	0.35	0.28	0.24	0.24
2,2,4-trimethylbenzene	0.13	0.28	0.54	0.18
isobutylene + *n*-but-1-ene	0.03	0.04	0.04	0.30
trans-but-2-ene	0.04	0.06	0.05	0.08
cis-pent-2-ene	0.12	0.16	0.11	0.18
n-hex-1-ene	0.03	0.06	0.03	0.05

abundance relative to isopentane in the tunnel air is significantly higher than the gasoline fuel compositions. The aromatic content relative to isopentane in the tunnel air is also markedly increased compared to the gasoline fuels. The two aromatic NMOC compounds most abundantly increased relative to isopentane are toluene and benzene.

Ratios of NMOC Compounds to Acetylene for 1982 Study Results. Experimental design of the 1982 sampling programs differed from the 1970 study in that outside tunnel ventilation air samples were simultaneously collected along with the tunnel samples. This air was used to dilute and ventilate the tailpipe emissions released from vehicles traveling through the tunnel. In the 1970 study, ratios to acetylene were determined from tunnel air samples with the justification that the concentrations observed were 10–15 times higher than outside air levels (*1*). In the 1982 study the average tunnel NMOC concentration of 4296 ± 696 ppb of C is just 8 times greater than the measured averaged outside air concentration of 507.2 ± 198.2 ppb of C. Averaged acetylene concentration for the tunnel and ventilation air samples were 160.7 ± 46.0 and 15.0 ± 7.0 ppb of C, respectively. The tunnel air to ventilation air ratio for acetylene is greater than 10, suggesting that sources other than vehicular tailpipe emissions are indeed contributing to the NMOC burden in the outside ventilation air. Consequently ratios to acetylene from the 1982 study results were determined after subtracting outside tunnel ventilation air compound concentrations from the tunnel compound concentration values. In this way, contributions from other sources of NMOC outside the tunnel were eliminated.

The vehicular ratios to acetylene for several NMOC compounds and sum of NMOC compounds are listed in Table V. For comparison the similar ratios to acetylene, determined for the 1970 study, are also included. From the table it is evident that all 1982 ratios to acetylene are larger than the 1970 values. These increases range from more than 500% for cyclohexane to as little as 3% for *m*-xylene. The sum of paraffin NMOC compounds to acetylene ratio increase of 54% is smaller than the nearly 90% increase in the sum of olefinic and sum of aromatic NMOC compounds to acetylene ratios. The unanimity of increase in the 1982 ratios demonstrates the reduced contribution of acetylene to the total NMOC concentration due to the selective removal by the vehicular-catalytic-converter system. The inconsistent increases of these

Table V. Selected Averaged NMOC Compound and Sum of NMOC Compounds to Acetylene Ratios for the 1982 and 1970 Lincoln Tunnel Results

compound	1982 ratio ± SD	1970 ratio ± SD
ethylene	2.67 ± 0.33	1.33 ± 0.14
propylene	0.78 ± 0.08	0.61 ± 0.07
isobutane	0.42 ± 0.05	0.34 ± 0.05
n-butane	1.21 ± 0.19	0.97 ± 0.12
isobutylene + *n*-but-1-ene	0.57 ± 0.08	0.34 ± 0.04
sum of C_4 olefins	1.06 ± 0.11	0.60 ± 0.07
isopentane	1.90 ± 0.28	1.25 ± 0.14
n-pentane	0.92 ± 0.14	0.62 ± 0.07
n-pent-1-ene	0.10 ± 0.01	0.07 ± 0.01
sum of C_5 olefins	0.82 ± 0.10	0.53 ± 0.08
3-methylpentane	0.47 ± 0.06	0.34 ± 0.04
n-exane	0.48 ± 0.07	0.36 ± 0.05
n-hex-1-ene	0.09 ± 0.1	0.03 ± 0.00
2,4-dimethylpentane	0.44 ± 0.04	0.34 ± 0.04
cyclohexane	0.28 ± 0.05	0.05 ± 0.01
3-methylhexane	0.32 ± 0.05	0.24 ± 0.04
2,2,4-trimethylhexane	0.36 ± 0.06	0.27 ± 0.05
benzene	1.32 ± 0.10	1.14 ± 0.40
toluene	1.89 ± 0.13	1.27 ± 0.23
p-xylene	0.31 ± 0.02	0.25 ± 0.03
m-xylene	0.72 ± 0.06	0.70 ± 0.15
o-xylene	0.46 ± 0.04	0.28 ± 0.04
p- + *m*-ethyltoluene	0.60 ± 0.07	0.38 ± 0.05
1,3,5-trimethylbenzene	0.17 ± 0.01	0.13 ± 0.02
formaldehyde	0.22 ± 0.18	
acetaldehyde	0.05 ± 0.04	
sum of paraffins	10.53 ± 1.30	6.81 ± 0.92
sum of olefins	6.03 ± 0.63	3.24 ± 0.32
sum of aromatics	9.58 ± 0.73	5.01 ± 0.70
sum of NMOC	26.0 ± 2.10	15.7 ± 1.87
NO_x	15.9 ± 4.9	6.13 ± 2.14
carbon monoxide	100.0 ± 4.5	63.40 ± 6.10

ratios from 1970 to 1982 are possibly due to both the selective removal of NMOC compounds by the vehicular-catalytic-converter system and gasoline composition changes during the 12-year period.

The improved precision of the 1982 ratios over the 1970 values probably results from the substraction of the outside tunnel ventilation air NMOC compound concentrations from those observed in the tunnel. The 1982 total NMOC to acetylene ratio precision of ±8.0% is a significant improvement over the 12.4% value of the 1970 ratio. The applicability of these ratios to estimate vehicular tailpipe emission contribution can be demonstrated by using data from the outside tunnel ventilation air sample taken on September 9, 1982. By use of the acetylene ratios given in Table V, the vehicular tailpipe contribution to the total NMOC burden can be estimated. The difference between the observed value and the estimated vehicular concentration is the contribution from other NMOC sources. To calculate estimated vehicular concentration, the observed acetylene concentration, in this example 12.9 ppb of C, is multiplied by the respective NMOC compound to acetylene ratios given in Table V. To demonstrate this, the propylene to acetylene ratio of 0.78 ± 0.08 is multiplied by 12.9 ppb of C to produce an estimated vehicular concentration of 10.1 ± 1 ppb of C. This calculated propylene concentration compares favorably to the observed value of 11.9 ppb of C and indicates that probably all of the propylene found in the outside tunnel air sample can be attributed to vehicular tailpipe emissions. Calculated vehicular concentration estimates for other NMOC compounds and the sums of paraffins, olefins, and aromatics for the September 9 sample are given in Table VI. The contribution from nonvehicular sources is given in the column labeled "difference". This column was obtained by subtracting the calculated vehicular concentration from

Table VI. Observed and Estimated Vehicular Concentrations for Selected NMOC Compounds and Sum of NMOC Compounds for the September 9, 1982, Outside Air Tunnel Ventilation Sample

compound	observed concn, ppb of C	calculated concn,[a] ppb of C	difference, ppb of C
ethane	31.3		31.3
propane	24.0		24.0
acetylene	12.9		
ethylene	25.8	34.4	−8.6
propylene	11.9	10.1	1.8
isobutane	21.7	5.4	16.3
n-butane	42.3	15.6	26.7
isobutylene + but-1-ene	5.1	7.3	−2.2
isopentane	50.3	24.5	25.8
n-pentane	26.3	11.9	14.4
pent-1-ene	1.4	1.3	0.1
3-methylpentane	9.4	4.1	5.3
2,2,4-trimethylpentane	8.4	4.6	4.8
benzene	18.2	17.0	1.2
toluene	34.7	24.4	10.3
p-xylene	6.0	4.0	2.0
m-xylene	13.7	9.3	4.3
o-xylene	8.4	5.7	2.7
m- + *p*-ethyltoluene	9.0	7.1	1.8
1,3,5-trimethylbenzene	3.6	2.2	1.4
sum of paraffins	316.4	135.8	180.6
sum of olefins	79.4	77.8	1.6
sum of aromatics	170.4	123.6	46.8
sum of NMOC	566.2	335.4	230.8

[a] Calculated concentration is obtained by multiplication of the observed acetylene concentration by the NMOC compound to acetylene ratios given in Table V.

the observed value. Looking at the difference column, the majority of NMOC compounds from other sources appears to be paraffins with some contribution of the aromatic compounds. Apparently all of the olefinic NMOC compounds could be attributed to vehicular tailpipe emissions. The most abundant individual paraffinic NMOC compounds include ethane, propane, *n*-butane, and isopentane. Nonvehicular concentrations of these compounds range from 24 to 31.3 ppb of C. Both ethane and propane are very minor components of vehicular tailpipe emissions, and their presence in the outside tunnel ventilation air sample is possibly the result of petroleum refinery activities and natural gas usage. Both *n*-butane and isopentane are in gasoline and could have been released to the ambient air by both gasoline spillage and gasoline evaporation processes. Even though other nonvehicular paraffinic and aromatic NMOC compounds are evident, it appears from the relative abundance of the *n*-butane and isopentane levels that evaporative emissions sources are more prevalent. Gasoline spillage appears to be a minor source in this outside tunnel ventilation air sample since low benzene and the combined *m*- and *p*-ethyltoluene concentrations are observed in the difference column. The most abundant nonvehicular aromatic compound is toluene, whereas the benzene concentration in the air sample can be attributed entirely to vehicular tailpipe sources.

As indicated earlier, all olefinic NMOC compounds appear to be attributable to vehicular tailpipe sources. In fact, the negative concentrations for ethylene and the combined isobutylene and 1-butene-1 peak suggest that the vehicular source over accounts for these compounds. The negative value could indicate loss of the very reactive olefinic compounds via reactions with ozone and the OH radical. The concentrations of O_3 and OH in ambient air during the 7:30–9:30 a.m. period however are expected to be quite small. The rather large −8.6 ppb of C ethylene concentration in the difference column of Table VI is difficult to explain. Perhaps this is the result of measurement error in the analytical system. Ethylene is the most volatile NMOC compound measured in these air samples. Care must be taken in the preconcentration step to prevent revaporization of the condensed ethylene compound before injection into the GC column system.

Summary and Conclusions

Detailed NMOC results are reported for a sampling program inside the Lincoln Tunnel. Included are averaged ratios to acetylene for selected NMOC compounds and sum of NMOC compounds along with standard deviations. Comparison of these data with similar data collected in 1970 indicated a factor of 4 reduction in NMOC levels. Since the ventilation rates of the tunnels have not been deliberately increased over the 12-year period, this factor of 4 reduction probably reflects reduced vehicular tailpipe emissions as the result of the use of catalyst-equipped vehicles. The factor of 4 reduction in NMOC levels compares well with the expected distribution of model year within the automobile fleet and the reduced vehicular emission rates as the result of the use of catalytic converters.

Acetylene abundance in the NMOC composition decreased significantly over the 12-year period. The somewhat reduced contribution of acetylene to the total NMOC concentration can be explained by the apparent preferred affinity the catalyst converter has for this compound. Lower acetylene concentrations result in higher NMOC compound and sum of NMOC compounds to acetylene ratios than those calculated in the 1970 tunnel study.

The most significant change in NMOC composition is a 4–5% increase of aromatic NMOC compounds at the expense of the paraffinic fraction. This would suggest that automobile tailpipe emissions have a slightly higher reactivity in 1982 than in 1970 when considered on a compositional basis. From the standpoint of photochemical ozone control strategy, the 1982 tunnel NMOC composition appears to be somewhat more reactive than the 1970 tunnel mixture due to the increased presence of the aromatic compounds. However, the most important impact on photochemical ozone control strategy is the significant decrease in total NMOC concentration. The averaged $NMOC/NO_x$ ratio of 1.77 observed in the 1982 tunnel study was somewhat lower than the 2.63 averaged value measurement in the 1970 study. this decrease in $NMOC/NO_x$ is consistent with the operation of the catalyst device. The catalytic converter is designed to oxidize NMOC and CO emissions and is not particularly effective with NO_x. Consequently, reduced NMOC levels result in lower $NMOC/NO_x$ ratios.

Unlike a dynamometer, the tunnel represents tailpipe NMOC emissions for only a limited number of vehicle operational conditions expected in typical urban driving patterns. Dynamometer studies can simulate urban driving patterns to investigate the NMOC compositional changes that occur. However, dynamometer results represent only the vehicles and the gasolines investigated. Tunnel ambient air however is representative of a large number of vehicles and gasolines. For this reason the NMOC composition and NMOC compound ratios to acetylene are useful to evaluate vehicular tailpipe contribution in urban and industrial areas.

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Registry No. NO_x, 11104-93-1; ethylene, 74-85-1; acetylene, 74-86-2; propylene, 115-07-1; isobutane, 75-28-5; *n*-butane, 106-97-8; isobutylene, 115-11-7; *n*-butene, 106-98-9; isopentane, 78-78-4; *n*-pentane, 109-66-0; *n*-pent-1-ene, 109-67-1; 3-methylpentane, 96-14-0; *n*-hexane, 110-54-3; *n*-hex-1-ene, 592-41-6; 2,4-dimethylpentane, 108-08-7; cyclohexane, 110-82-7; 3-methylhexane, 589-34-4; 2,2,4-trimethylpentane, 540-84-1; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; *m*-xylene, 108-38-3; *o*-xylene, 95-47-6; *p*-ethyltoluene, 622-96-8; *m*-ethyltoluene, 620-14-4; 1,3,5-trimethylbenzene, 108-67-8; formaldehyde, 50-00-0; acetaldehyde, 75-07-0; carbon monoxide, 630-08-0; 1,2,4-trimethylbenzene, 95-63-6; *trans*-but-2-ene, 624-64-6; *cis*-pent-2-ene, 627-20-3.

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